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The Effects of Different Calcination Parameters on CCTO Formation

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Abstract **-** Dielectric material $CaCu_3Ti_4O_{12}$ (CCTO) was prepared by solid state technique. $CaCO_3$, TiO_2 and CuO powders were mixed thoroughly in a ball mill for an hour. The mixed powder was calcined at 800 and 900 ^{o}C for different durations. The calcined samples were subjected to XRD phase analysis and SEM observation. All the samples were sintered at 1050 ^{o}C for 24 hours, before dielectric constant measurement was done. The effects of different calcination parameters on phase formation, microstructures, and dielectric constant were reported. XRD results show the different phase formations, and the CCTO single phase was first detected for the sample calcined at 900 ^{o}C for 6 hours. Increasing the temperature and duration enhances the density, dielectric constant value and the grain growth was observed. The CCTO single phase with the highest dielectric constant was obtained by calcination at 900 ^{o}C for 12 hours.

Keywords: CCTO, Calcination, Phase Formation, Microstucture, Dielectric Constant

I. INTRODUCTION

Recently, $CaCu_3Ti_4O_{12}$ (CCTO) was discovered to possess one of the largest static dielectric constant ever measured, reaching nearly ε_r ~ 80 000 for single crystal samples and 10 000 for bulk material at room temperature [1, 2, 3]. The higher the dielectric constant, the more charge it can store, and the smaller electronic circuits can be designed. Unlike most dielectric materials, CCTO remains its high dielectric constant over a wide range of temperatures, from 100 to 600 K (-173 to 327 ^{o}C). This properties making the CCTO ideal for a wide range of applications.

However, the nature on how the CCTO represents such high dielectric constant and its abrupt changes at 100 and 600 K are still not well understood [4]. Many researchers claimed that factor such as grain boundary, presence of twin boundaries or other planar defects and displacement of Ti ions could be the reasons for those changes [1, 5]. More extensive researches are needed for a more comprehensive explanation.

The dielectric properties are very sensitive to processing [6]. In this project, the CCTO was prepared by solid state technique, and the processes involve are mixing, calcination, compaction and sintering. Some researchers are concentrating on sintering process, because there are important to find the right sintering parameter to ensure the correct microstructure with high dielectric constant property will be obtained [6, 7, 8]. But the process of calcinations also important, because in CCTO preparation, the CCTO single phase form can be obtained directly after calcinations [6, 9]. Based on thermal analysis, a research was carried out to investigate the right calcinations temperature and duration to fabricate CCTO with clear microstructure and high dielectric constant.

II. METHODOLOGY

CCTO samples were prepared by a conventional solid state method. High purity of $CaCO_3$ (Aldrich, 99%), TiO_2 (Merck, 99%) and CuO (Aldrich, 99%) were used as starting materials. A stoichiometric reagents were mechanically ball milled for 1 hour using zirconia balls. A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. The powder was calcined in

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air at 800 and 900 ^{o}C for different durations i.e. 6, 9, 12 and 15 hours. The samples were coded according to calcinations temperature and duration. The calcined samples were subjected to XRD phase analysis and FESEM (Zeiss SUPRA 35VP) observation. Cylindrical specimens with 5 mm diameter and approximately 0.5 - 1 mm thick were pressed. The green pellets were sintered in air at 1050 ^{o}C for 24 hours, with a heating rate of 5 ^{o}C/minutes. The samples for measuring dielectric constant were polished to ensure surface flatness and then painted with silver paste on both surfaces as electrodes. The measurement was done at room temperature by Philips RCL meter PM 6303 at 1 kHz frequency.

III. RESULTS AND DISCUSSION

Figures 1 and 2 represent the XRD analysis for all the samples. In figure 1, the calcination was carry out at 800 ^{o}C for 6,9,12 and 15 hours. It can be seen from the acquired result that instead of CCTO phase, there were few raw materials peak were detected. These raw materials are not completely reacted and the formation of $CaTiO_3$ phase also identified. Calcination at 900 ^{o}C (Figure 2) transforms all the raw materials into CCTO single phase.

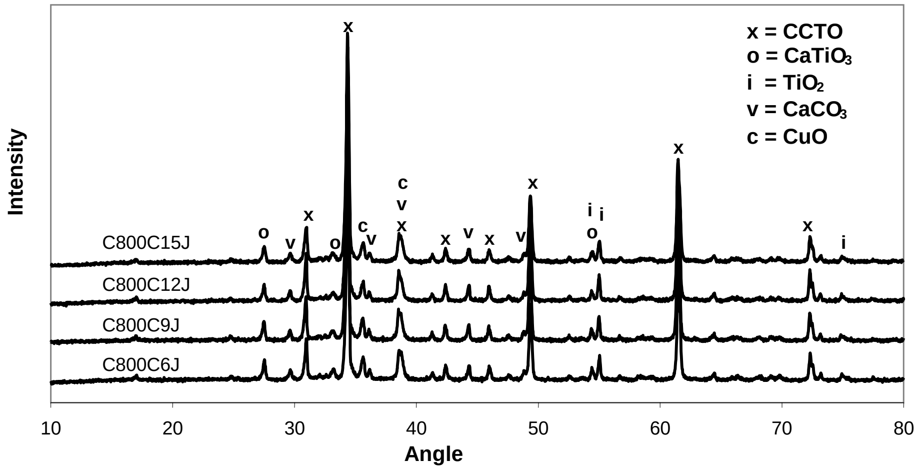


Figure 1: XRD analysis for samples calcined at 800 ^{o}C.

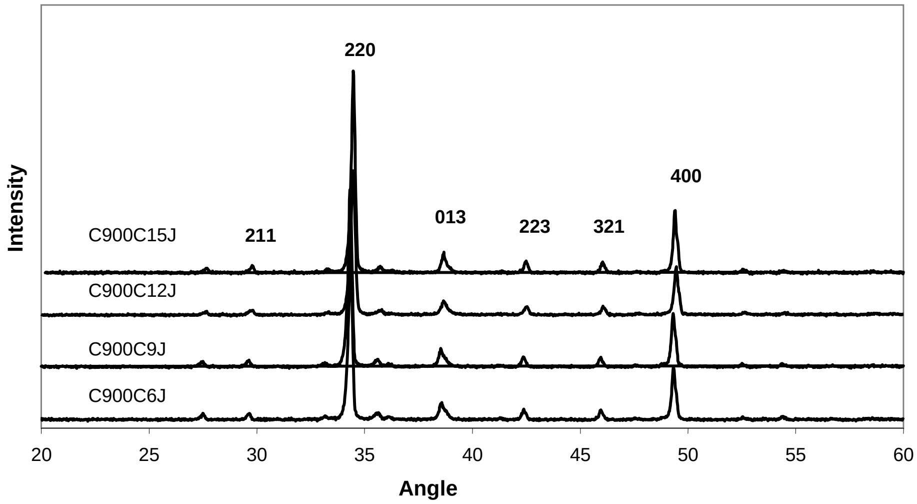
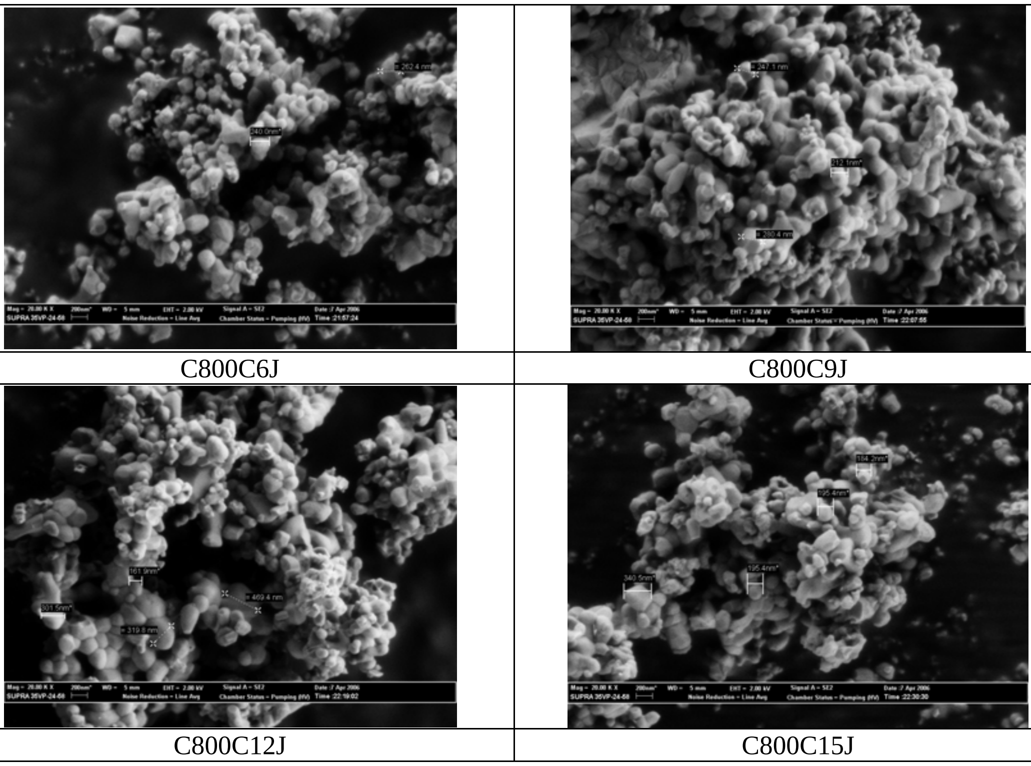


Figure 2: XRD analysis for samples calcined at 900 ^{o}C.

Figure 3 and 4 show the SEM micrograph for all the samples. The micrograph reveals that the CCTO grain was spherical in shape. The same shape was reported by other researcher [10]. They were comparing the particle morphology obtained by solid state and organic precursor techniques. Figure 3 shows that the grain sizes are consistent and which are not influenced by calcination duration. The particles size was in range of 0.05 – 0.2 µm. But the grains were quite expands (0.2 – 0.5µm) when subjected to higher calcinations temperature (Figure 4). Calcinations at lower temperature can not compose the raw materials into desired compounds, but if the temperatures are very high, the abnormal grain growth will occurred. So, the optimum temperature and duration for calcination process must be decided in order to obtain the desired microstuctural and dielectric properties. In this case, 900 ^{o}C are very appropriate temperature in calcining CCTO due to CCTO single phase formed. The right calcinations duration should be decided based on the dielectric measurement.



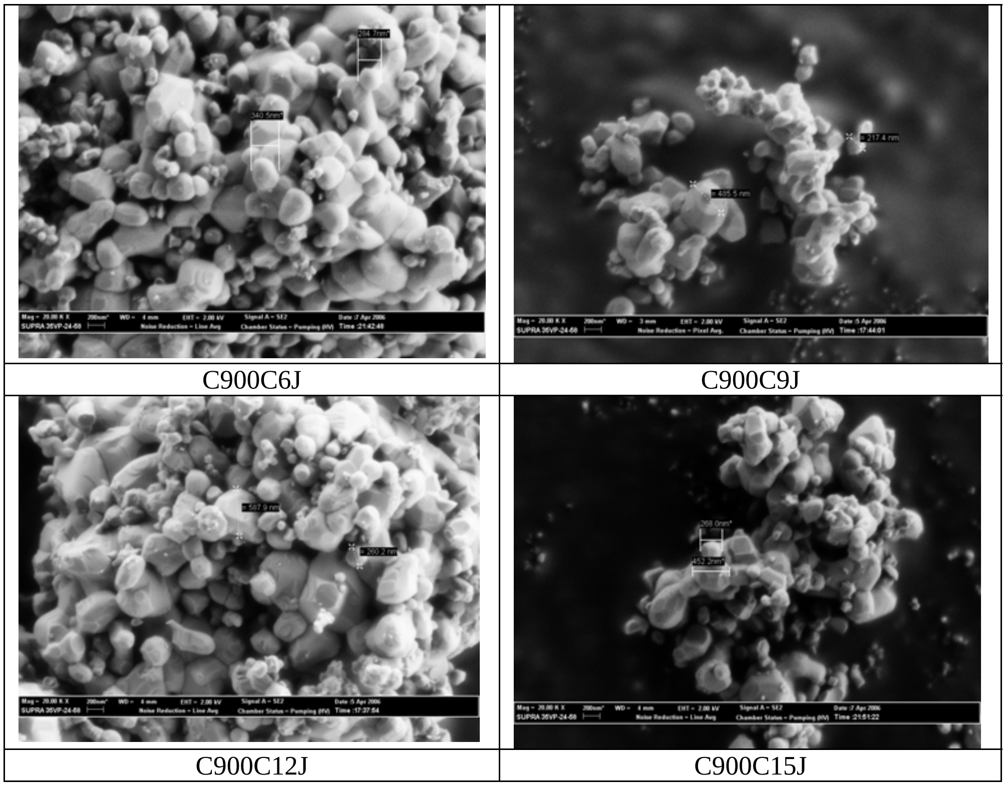
C800C6J

C800C9J

C800C12J

C800C15J

Figure 3: SEM micrograph for samples calcined at 800 ^{o}C.



C900C6J | C900C9J

C900C12J | C900C15J

Figure 4: SEM micrograph for samples calcined at 900 °C.

Figure 5 shows the results of dielectric constant measurements for all the samples. Longer calcinations time increases the dielectric constant, up to maximum value at 12 hours, then tends to decrease for the samples calcined at 15 hours. The samples calcined at 900 °C gave the higher dielectric constant value compared to samples calcined at lower temperature. The maximum value (21922) was obtained for the sample C900C12J. But, the next processes such as compaction and sintering might be altered the properties of CCTO.

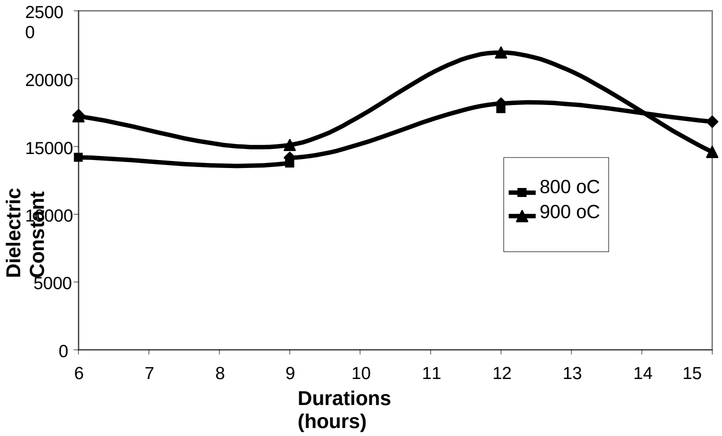


Figure 5: Dielectric constant value measured at 1 kHz for the samples calcined at different temperatures and durations.

IV. CONCLUSION

The calcination at 900 °C directly produces a CCTO single phase. The grains were spherical in shape with the range sizes of 0.05 – 0.5 μm. Increasing the calcination temperature enhances the grain sizes. Calcinations at longer time and higher temperature increase the dielectric constant. The highest dielectric constant value (21922) was obtained for the sample C900C12J.

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